

Determination of nucleation rates near the critical point

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Abstract

The nucleation rates derived for the condensation from a supersaturated vapor are examined both in the classical theory and in the modern coarse-grained field theory. By virtue of the scaling variable λ_Z it is shown that the method of steepest descent is irrelevant to evaluate the nucleation rate in the proximity of the critical point in the capillary approximation. If the logarithmic corrections to the activation energy of a droplet are taken into account, then the calculated nucleation rates provide an adequate description of the liquid-gas phase transition both near and out of the critical range.

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The problem of homogeneous nucleation has been intensively investigated both theoretically and experimentally (see, e.g., [1–3] and references therein). The first theoretical approach to it, which is often referred to as classical nucleation theory, was worked out about 50 years ago mainly by Becker and Döring [4] and Zeldovich [5]. Later on the classical nucleation theory was generalized to a system of arbitrarily many degrees of freedom by Landauer and Swanson [6] and to the field theories by Cahn and Hilliard [7] and Langer [8,9]. Langer pointed out that the coarse-grained procedure can be efficiently performed near the critical point where the radius of critical fluctuations is larger than the characteristic correlation length.

Both classical and modern coarse-grained field theory assumes that the decay of an initially homogeneous metastable state should proceed via the formation of nucleated clusters of a new, stable state. The rate of relaxation of the metastable state, or nucleation rate, is given by the formula

$$I = I_0 \exp(-\beta \Delta F_c) . \quad (1)$$

Here I_0 is the preexponential factor, $\beta \equiv (k_B T)^{-1}$, k_B is Boltzmann's constant, T is the temperature of the system, and ΔF_c is the excess free energy of the critically large cluster in the system. Even though the prefactors in both theories have different expressions, the numerical results for condensation from the supersaturated vapor [10] are very similar. In principle, it is possible to show [11] that under the certain assumptions the prefactor derived in the classical theory may be obtained in a form equivalent to that of the field theory. To test the predictions of the nucleation theories a number of experiments on the separation of binary fluids near the critical point [12,13] have been performed. It turned out that the critical systems were more stable than it was expected from the theoretical calculations. To explain this difference between theory and experiment Binder and Stauffer [14,15] argued that since the experimentalists measured the completion time of the transition, one has to consider both droplet formation and droplet evolution, growth and shrinkage, during the relaxation process. Near the critical point droplets grow very slowly and this circumstance

decelerates the completion of the phase transition. A detailed description of the nucleation kinetics in near-critical fluids similar to the theory of coagulation by Lifshitz and Slyozov [16,17] has been developed by Langer and Schwartz [18]. The overall reaction rate was found to be much lower than the nucleation rate alone.

In the present paper we would like to show that the nucleation rate itself calculated in the capillary approximation near the critical point is overestimated. Therefore, the agreement between theory and experiment should be even better. For the sake of simplicity, we will consider first the application of the classical nucleation theory to a first-order phase transition with only one order parameter, for instance, condensation from the supersaturated vapor.

The excess of the Helmholtz free energy due to the formation of a spherical droplet of radius R is equal in the capillary (or thin wall) approximation [17] to the sum of the bulk and the surface energies

$$\Delta F(R) = -\frac{4\pi}{3}R^3\Delta p + 4\pi R^2\sigma , \quad (2)$$

containing the difference in pressures inside and outside the droplet Δp and the surface tension σ . Minimization of ΔF with respect to the radius yields the energy of the critically large droplet $\Delta F_c = \frac{4}{3}\pi R_c^2\sigma$, where the critical radius is given by Laplace's formula $R_c = 2\sigma/\Delta p$. Using the reduced variables [19] $\lambda_Z = R_c \sqrt{4\pi\sigma\beta}$ and $r = R/R_c$, we have

$$\beta\Delta F = -\frac{2}{3}\lambda_Z^2 r^3 + \lambda_Z^2 r^2 \quad (3)$$

and

$$\beta\Delta F_c = \frac{1}{3}\lambda_Z^2 . \quad (4)$$

As first shown by Zeldovich [5], the size distribution function of droplets $f(R)$ obeys the Fokker-Planck kinetic equation

$$\frac{\partial f}{\partial t} = -\frac{\partial J}{\partial R} , \quad (5)$$

where

$$J = -B \frac{\partial f}{\partial R} + A f \quad (6)$$

is a so-called current in the size space, containing the diffusion and the drift coefficients B and A . The solution of Eq. (5) corresponding to $J = J_0 = 0$ is a well-known canonical distribution $f_0(R) \propto \exp(-\beta\Delta F)$. In terms of the ratio $f(R)/f_0(R)$, Eq. (6) may be rewritten as

$$J = B f_0(R) \frac{\partial}{\partial R} \left(\frac{f(R)}{f_0(R)} \right) . \quad (7)$$

The theory of first-order phase transitions is based on the requirement of the steady-state flux $J = J_{ss} = \text{const}$. In the region of small r the distribution function $f(R)$ is very close to the equilibrium distribution function $f_0(R)$, whereas it diminishes quickly for $r \geq 1$. These boundary conditions represent the constant replenishment of the stock of small droplets because of the thermodynamic fluctuations and the fact that droplets of supercritical sizes are removed from the system and merge into the new phase. The steady-state solution of Eq. (7) that satisfies both boundary conditions reads

$$J_{ss}^{-1} = \int_0^\infty \frac{dR}{B f_0(R)} . \quad (8)$$

In order to evaluate the integral analytically it is usually mentioned that the integrand has a very sharp maximum at $R = R_c$ due to the maximum of the activation droplet energy at this point. Therefore, one may replace the activation energy near the critical radius by its harmonic approximation

$$\begin{aligned} \beta\Delta F &= \beta(\Delta F)_{R=R_c} + \frac{1}{2}\beta \left(\frac{\partial^2 \Delta F}{\partial R^2} \right)_{R=R_c} (R - R_c)^2 \\ &= \beta\Delta F_c - \lambda_Z^2(r - 1)^2 \end{aligned} \quad (9)$$

and then apply the method of steepest descent. We have

$$J_{ss} = \frac{B(r_c) f_0(r_c)}{R_c} \sqrt{-\frac{\beta}{2\pi} \left(\frac{\partial^2 \Delta F}{\partial r^2} \right)_{r=r_c}} = \frac{B(1) f_0(1)}{R_c} \frac{\lambda_Z}{\sqrt{\pi}} . \quad (10)$$

Mathematically, the assumption that $\Delta F(r)$ has a sharp maximum at $r_c = 1$ means that

$$\left[\sqrt{\beta |\Delta F''(1)|} \right]^{-1} \ll 1 , \quad (11)$$

where $\Delta F''$ denotes the second derivative of ΔF with respect to the reduced radius r .

It is easy to see that in the capillary approximation

$$\beta |\Delta F''(1)| = 2\lambda_Z^2 . \quad (12)$$

Our next step is to determine the dependence of the similarity number λ_Z on the critical exponents provided the temperature of the system approaches the critical one.

As functions of $\theta = 1 - T/T_c$, the thermodynamic quantities needed for our analysis have the following power-law approximations in the vicinity of the critical point:

$$\sigma \sim \theta^{\mu'} , \quad \Delta p \sim \theta^{\beta' \delta'} . \quad (13)$$

In classical theory the critical exponents β' and δ' are equal to $1/2$ and 3 , respectively. The measured value of the exponent μ' lies in the range 1.22 – 1.29 [20] and we will use $\mu' = 1.25$ in our further calculations. Thus the critical radius tends to infinity at a critical temperature as $\theta^{(\mu' - \beta' \delta')} = \theta^{-1/4}$. The similarity number near the critical temperature obeys the power law

$$\lambda_Z = R_c \sqrt{4\pi\sigma\beta} \sim \theta^{(\frac{3\mu'}{2} - \beta' \delta')} = \theta^{3/8} \quad (14)$$

It is clear that the parameter λ_Z tends to zero at $T \rightarrow T_c$ and that the criterion (11) is not fulfilled. Therefore, in the thin wall approximation the method of steepest descent is not applicable to the evaluation of the nucleation rate near the critical point.

In the semiphenomenological droplet model worked out by Fisher [21] the activation free energy includes also the curvature term related to the small fluctuations in the shape of the droplet which do not change both the volume and the surface area of the droplet

$$\Delta F^F(R) = -\frac{4}{3}\pi R^3 \Delta p + 4\pi\sigma R^2 + 3\tau\beta^{-1} \ln \frac{R}{r_0} . \quad (15)$$

Here τ is the Fisher critical exponent, which is about 2.2 , and r_0 is the radius of the smallest droplet in the system. It is worth noting that the spherical harmonic excitations of a droplet

(Goldstone modes) have been calculated [8,22] also in the field theory. These calculations lead to the appearance of the logarithmic term in the expansion of the free-energy density, similar to the curvature term in Eq. (15), with the critical exponent $\tau = 7/3$. Then in the harmonic approximation

$$\beta\Delta F^F = \beta\Delta F_c^F - \frac{9\tau + 2\lambda_Z^2}{2} (r - 1)^2 , \quad (16)$$

$$\beta\Delta F_c^F = -\tau + \frac{\lambda_Z^2}{3} + 3\tau \ln \frac{R_c^F}{r_0} . \quad (17)$$

Note that the critical radius R_c^F appearing in Eq. (17) is not the same as that given by Laplace's formula, but should be determined by the solution of cubic (with respect to R) equation. Now

$$\beta|[\Delta F^F(1)]''| = 9\tau + 2\lambda_Z^2 \quad (18)$$

and the method of steepest descent is relevant since the criterion (11) is fulfilled:

$$(9\tau + 2\lambda_Z^2)^{-1}_{\lambda_Z \rightarrow 0} \longrightarrow (9\tau)^{-1} \ll 1 . \quad (19)$$

Performing the saddle-point integration in Eq. (8), one can find the nucleation rate in the droplet model approach

$$J_{ss}^F = \frac{B^F(1)f_0^F(1)}{R_c^F} \sqrt{\frac{9\tau + 2\lambda_Z^2}{2\pi}} . \quad (20)$$

To compare the analytical expressions given by Eqs. (10) and (20) with the numerical solutions of Eq. (8), we plot in Fig. 1 the ratio $(J_{ss})_{\text{numeric}} / (J_{ss})_{\text{analytic}}$ versus $\lambda_Z = R_c \sqrt{4\pi\sigma\beta}$ calculated both in the capillary approximation and in the Fisher droplet model. We see that formula (20) gives us values of the nucleation rate J_{ss} that agree with the results of numerical calculations by Eq. (8) within the 5% accuracy limit even for very small values of λ_Z . In contrast, in the capillary approximation presented by Eq. (10), significant deviations from the numerical results start already at $\lambda_Z = 2$, which is assigned to a system rather far from the critical point. Thus the value $\lambda_Z = 2$ may be considered as a limit of applicability of the

classical expression (10) for the nucleation rate. At larger values of the similarity number both analytical expressions (10) and (20) fit well to the results of numerical calculations.

The errors introduced by the method of steepest descent have been calculated numerically [23] for the condensation of a gas. It was found that the errors are negligibly small except for the smallest critical droplets and for the smallest values of the activation energy of the critical droplet. We show that this error can be parametrized by the single scaling variable λ_Z . Our analysis is valid for the Langer theory [9] also, in which the prefactor I_0 is shown to be a product of the dynamical and statistical prefactors κ and Ω_0 , respectively,

$$I_0 = \frac{|\kappa|}{2\pi} \Omega_0 . \quad (21)$$

The dynamical prefactor describes the exponential growth rate of the unstable mode at the saddle point. It is related to the single negative eigenvalue λ_1 of the generalized mobility matrix $M_{ij} = \partial^2 \Delta F / \partial \xi_i \partial \xi_j$, where $\{\xi_i\}$ is a set of macroscopic variables describing the system. The integration over a plane containing the saddle point is performed by the method of steepest descent and the statistical prefactor becomes

$$\Omega_0 = \mathcal{V} \left(\frac{2\pi}{\beta |\lambda_1|} \right)^{1/2} \left[\frac{\det(\beta M_0 / 2\pi)}{\det(\beta M' / 2\pi)} \right]^{1/2} , \quad (22)$$

where \mathcal{V} is the available phase-space volume of the saddle point, the index 0 denotes the metastable state, and a prime indicates that the negative eigenvalue λ_1 as well as the zero eigenvalues of the matrix M_{ij} is omitted. For the process of vapor condensation the simplified model contains only the order parameter. From the definition of the mobility matrix it follows that $-\beta \lambda_1 = 2\lambda_Z^2$ [cf. Eq. (12)]. Therefore, Eq. (22) cannot be applied in the capillary approximation for the liquid-gas system near the critical point because the criterion (11) is violated. To calculate the nucleation rate in the critical region one has either to evaluate the integral numerically or to insert the logarithmic corrections [8,22] mentioned above in the activation energy of a droplet *before* the steepest-descent evaluation of the integral. In the latter case this curvature term will play a crucial role in the determination of the saddle point for the free-energy functional. This is the last important point in our discussion. Equation

(1) can be rewritten also [8] via the imaginary part $\text{Im } \mathcal{F}$ of the analytic continuation of the free-energy density to the metastable state

$$I = \frac{\beta|\kappa|}{\pi} \text{Im } \mathcal{F}, \quad (23)$$

and the evaluation of $\text{Im } \mathcal{F}$ has been widely discussed in the literature. Sometimes $\text{Im } \mathcal{F}$ has a form [18] like $x^\tau \exp(-x^2)$, where the dimensionless variable x^2 corresponds to the activation energy of a critical droplet times β , and the saddle point is calculated *in the capillary approximation*. In the context of a steepest descent this implies that the term with the logarithmic corrections x^τ is considered as a slowly varying part of the integrand in the vicinity of saddle point. Therefore, these corrections are added to the activation energy *after* the saddle-point evaluation of the integral and the nucleation rate is overestimated again near the critical point.

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FIGURES

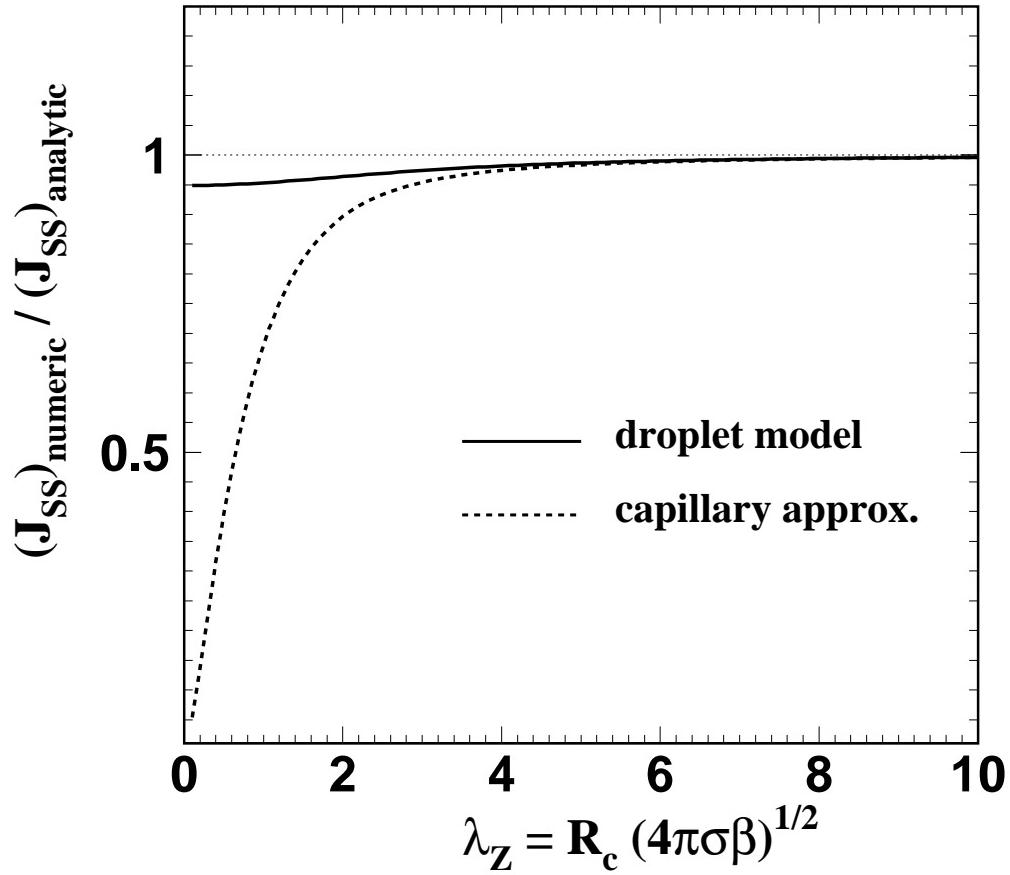


FIG. 1. Ratio $(J_{ss})_{\text{numeric}} / (J_{ss})_{\text{analytic}}$ versus the parameter $\lambda_Z = R_c (4\pi\sigma\beta)^{1/2}$ corresponding to the Fisher droplet model (solid line) and to the capillary approximation (dashed line).